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VOLTAGE FLUCTUATIONS AT SODIUM BETA' ALUMINA/MERCURY  
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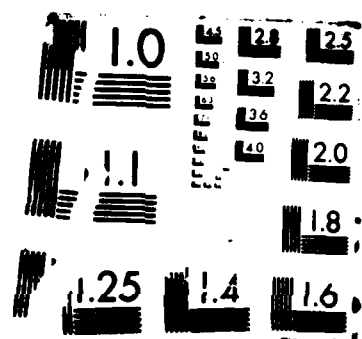
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Voltage fluctuations at mercury sodium Beta<sup>11</sup> alumina ceramic electrode interfaces have been investigated over frequencies ranging from  $10^{-3}$  to  $3 \times 10^4$  Hz. Noise voltages in the absence of current can be explained by Nyquist and interfacial chemical reaction noise. The activation energy of the reaction noise rate constant is determined to be 0.29 eV, which suggests that diffusion of the sodium ions in the electrolyte dominates the reaction. In the presence of a decomposition current, the low frequency noise varies as  $f^{-1.5}$ . After current flow, the noise voltage decays and can be observed for some tens of hours. Both current and post current noise signals suggest conductivity fluctuations arising from diffusion of the mobile sodium ions. Fitting experimental data to the diffusion and decay equations yields a diffusion constant of  $1.8 \times 10^{-6}$  cm<sup>2</sup>/sec and a characteristic length equal to the bulk sample length. (Key words)

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# VOLTAGE FLUCTUATIONS AT SODIUM $\beta''$ ALUMINA/MERCURY ELECTRODES

by

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## ABSTRACT

Voltage fluctuations at mercury/sodium  $\beta''$  alumina ceramic electrode interfaces have been investigated over frequencies ranging from  $10^{-3}$  to  $3 \times 10^4$  Hz. Noise voltages in the absence of current can be explained by Nyquist and interfacial chemical reaction noise. The activation energy of the reaction noise rate constant is determined to be 0.29 eV, which suggests that diffusion of the sodium ions in the electrolyte dominates the reaction. In the presence of a decomposition current, the low frequency noise varies as  $f^{-1.5}$ . After current flow, the noise voltage decays and can be observed for some tens of hours. Both current and post current noise signals suggest conductivity fluctuations arising from diffusion of the mobile sodium ions. Fitting experimental data to the diffusion and decay equations yields a diffusion constant of  $1.8 \times 10^{-6}$  cm<sup>2</sup>/sec and a characteristic length equal to the bulk sample length.

## I. INTRODUCTION

Mercury electrodes are used in Na  $\beta''$  alumina cells as cathodic acceptors to prepare sodium amalgam by Coulombic titration or as anodic donors to test voltage breakdown in solid electrolyte

membranes(1,2). In such devices the mercury electrode forms a blocking contact. Very high electrical resistance is expected if the ionic current direction is designated to inject cations into the  $\beta''$  alumina membrane. Voltage fluctuation investigations(3,4) on the mercury-sodium  $\beta''$  alumina contact have detected a relaxation noise occurring at around 100 Hz which is attributed interfacial reaction noise. The present work examines in greater detail the contact noise characteristics and extends the measurements to the presence of current. It may be expected that in a solid electrolyte system with blocking electrodes, an ionic current will build high space charge densities at the electrode-electrolyte interface, which may lead to polarization and breakdown of the solid electrolyte and affect noise generation processes.

## II. EXPERIMENTAL

Two-terminal cells are prepared by epoxying a rectangular sodium  $\beta''$  alumina ceramic sample between plastic tubes which act as reservoirs of mercury. The Na  $\beta''$  alumina sample is obtained from Ceramtec, Inc. with chemical composition 90.4%  $\text{Al}_2\text{O}_3$ , 8.85%  $\text{Na}_2\text{O}$ , 0.75%  $\text{Li}_2\text{O}$  and in dimensions of  $0.8 \times 0.4 \times 0.5 \text{ cm}^3$ . The ceramic was baked at  $800^\circ\text{C}$  in open air before use to remove moisture and organic contamination.

Voltage fluctuations are measured with the contacts connected to the input of a PAR 113 preamplifier. The output of the preamplifier

is analyzed digitally using A/D conversion and FFT program on an on-line computer. The spectral measurements cover the frequency range from  $10^{-3}$  to  $3 \times 10^4$  Hz.(3,5)

Current is supplied from a filtered battery source and through a 100 Kohm series resistor. Current noise measurements usually start about one hour after switching on the current, in order to reach a stable current condition. At that time the cell is heavily polarized.

### III. NOISE IN THE ABSENCE OF CURRENT

Similar to (3), the noise spectrum of a mercury-Na  $\beta''$  alumina contact consists of (i) Nyquist noise at high frequencies corresponding to the resistance of the  $\beta''$  alumina ceramic electrolyte; (ii) a relaxation noise in the mid-frequency portion; and (iii) excess low frequency noise which decreases gradually with storage time. In the present experiments contact noise is not measurable above internal amplifier noise at frequencies smaller than about 0.3 Hz for aged samples.

The temperature dependence of noise spectra observed from a two-week aged cell are shown in Figure 1. The relaxation noise near 100 Hz increases with decreasing temperature and shifts to lower frequencies. If chemical noise of a single species reaction is assumed, we may write the noise voltage spectral density  $S_v$  as (3)

$$\frac{S_v}{V^2} = \frac{S_I}{I^2} = \frac{4}{N} \frac{k_f}{k_f^2 + \omega^2} \quad (1)$$

where  $N$  is the average number of reacting species,  $k_r$  is the rate constant,  $\omega$  is the angular frequency and  $V = ZI = ZNek_r$  where  $Z$  is the impedance of the system and  $e$  is the electronic charge. Supposing  $Z$  is a constant in the measuring frequency range, which seems reasonable since only low noise levels are observed beyond the mid-frequency noise relaxation, we obtain

$$S(V, f) = \frac{C k_r^3}{k_r^2 + \omega^2} \quad (2)$$

$$C = 4 N e^2 Z^2$$

Fitted curves are shown in Figure 1. The smaller slope beyond the characteristic frequency observed here than calculated by Equation (2) can generally be interpreted in terms of a distribution of reaction species or relaxation times. The temperature dependence of the rate constant is shown in Figure 2. Linear least square calculation gives

$$k_r = 1.98 \times 10^8 \exp(-0.29 \text{ eV}/kT) \quad (3)$$

The activation energy of the chemical reaction, 0.29 eV, agrees with published conductivity and diffusion data for Na $\beta$  alumina, suggesting that diffusion of the mobile ions in the electrolyte dominates the chemical reaction process at the interface.

#### IV. CURRENT NOISE

When d.c. voltages are imposed on a solid electrolyte cell with



ion blocking electrodes, only temporary polarization and impurity currents are present, in addition to any electronic current. However, if the voltage is increased beyond the decomposition potential of the solid electrolyte, a decomposition current is generated, which may decrease with time due to surface passivation of the solid electrolyte by electrolytic deposition. A quasi-equilibrium current of 0.45 microamperes can be maintained in the present cell at 10 d.c. volts and at room temperature. Figure 3 illustrates a typical current noise spectrum which shows  $f^{-1.5}$  dependence characteristic of diffusion noise (6) below 10 Hz. The same contact reaction noise shown in Figure 1 is also apparent.

Decaying noise voltages are observed for periods of some tens of hours after switching off the current. In general, the spectral shape is similar to that of current noise, but the low-frequency diffusion noise level decreases with time. It appears that the ion concentration gradient produced by the applied voltage diffuses towards a uniform spacial distribution.

Similar concentration gradient noise decay observed in  $\beta$  lead fluoride by Kleinpenning and Peters (7) is described by an exponentially time-dependent equation. The diffusion noise level is shown to be proportional to  $\exp(-t\pi^2 D/L^2)$  where  $D$  is the diffusion constant and  $L$  is the sample length. The 15- and 48-hour noise data obtained here can be fitted by

$$S(V, 0.1 \text{ Hz}) = 2.7 \times 10^{-11} \exp(-2.8 \times 10^{-5} t) \quad (4)$$

where  $t$  is the setting time in seconds. This fit gives a relaxation time of  $3.6 \times 10^4$  sec. and for the sample length, 0.8 cm, the diffusion constant is calculated to be  $D = 1.8 \times 10^{-6} \text{ cm}^2/\text{sec}$ , which agrees with literature values.

According to Van Vliet and Fasset(6), the fluctuation in  $N$  particles due to one dimensional diffusion has the spectrum

$$S_n = \langle \Delta N^2 \rangle L^2 [1 - \exp(-r)(\cos r + \sin r)] / Dr^3 \quad (5)$$

$$r = L(\omega/2D)^{1/2}$$

where  $\langle \Delta N^2 \rangle$  is the total variance,  $L$  is a characteristic length and  $D$  the diffusion constant. Assuming Poisson statistics,  $\langle \Delta N^2 \rangle = N$  the voltage fluctuations are

$$S(V, f) = C' [1 - \exp(-r)(\cos r + \sin r)] / r^3 \quad (6)$$

$$C' = L^2 V^2 / DN$$

Summing the reaction, diffusion and Nyquist noise terms yields

$$S(V, f) = S(V, f)_{\text{reaction}} + S(V, f)_{\text{diffusion}} + S(V, f)_{\text{Nyquist}}$$

$$= Ck_f^3 / (k_r^2 + \omega^2) = C' [1 - \exp(-r)(\cos r + \sin r)] / r^3 + 4kT\text{Re} \quad (7)$$

where  $\text{Re}$  is the real part of the impedance. Inserting  $L=0.8$  cm and  $D=1.8 \times 10^{-6} \text{ cm}^2/\text{sec}$ , the curves given by Equation (7) are the solid

lines in Figure 3. These results show that the diffusion noise contribution decreases with setting time, while the contact reaction noise and the bulk Nyquist noise remain unchanged.

## V. DISCUSSION

These experimental results and calculations indicate interfacial reaction noise at the mercury/sodium  $\beta''$  alumina contact in the absence of current. From thermodynamic considerations there seems to be no bulk chemical reactions which can be expected between the mercury and sodium  $\beta''$  alumina at these experimental temperatures. As supposed in (4), the interfacial reaction involved here may be attributed to formation of intermediate sodium-mercury species, or partial amalgamation at the interface between mercury and sodium  $\beta''$  alumina. Open circuit voltages of 2.2-2.4 V have been observed between mercury and sodium electrodes at 350°C and the cathodic amalgamation reaction was supposed(8). The diffusion-dominated reaction noise observed here may reasonably support the speculation that the origin of the interfacial reaction noise arises from partial amalgamation. Diffusion is associated with supplement of sodium ions for the amalgamation reaction.

The current and post-current noise spectra show excess noise at low frequencies characteristic of  $-1.5$  frequency dependence. The experimental spectra can be well fitted with Equation (7), indicating a summation of chemical reaction noise, diffusion noise and Nyquist noise. The diffusion noise calculation confirms the diffusivity and

characteristic length deduced here and in previous studies(3,9). The calculated results suggest a characteristic frequency for diffusion noise ( $r=1$  in Equation 5) of  $9 \times 10^{-7}$  Hz.

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\* On leave from Shanghai Institute of Ceramics, Chinese academy of Sciences.

## REFERENCES

1. C. K. Kuo and S. T. Li, Ceram. Intern. 7, 98 (1981).
2. M. W. Breiter, N. S. Choudhury and E. L. Hall, J. Electrochem. Soc., 133, 2064 (1986).
3. J. J. Brophy and S. W. Smith, J. Appl. Phys. 58, 351 (1985).
4. C. K. Kuo and J. J. Brophy, submitted to 6th International Meeting on Solid State Ionics.
5. S. W. Smith, Rev. Sci. Instrum. 56, 159 (1985).
6. K. M. Van Vliet and J. R. Fassett, "Fluctuation Phenomena in Solids", R. E. Burgess (ed.), Academic Press, New York (1965), 268.
7. T. G. M. Kleinpenning and C. A. J. Peters, Phys. Stat. Sol. (a) 51, K105 (1979).
8. N. S. Choudhury, J. Electrochem. Soc. 133, 425 (1986).
9. J. J. Brophy and S. W. Smith, in "Noise in Physical System and 1/f Noise-1985", A. D'Amico and P. Mazzetti (eds), 243, Elsevier Science Publishers B. V. (1986).

## FIGURE CAPTIONS

Figure 1. Noise spectra in the absence of current; the solid lines are obtained by fitting with Equation (2).

(a) 274.4°K, Nyquist noise =  $2.25 \times 10^{-16} \text{ V}^2/\text{Hz}$ ,

Fitting parameters:  $k_r = 1600 \text{ sec}^{-1}$  and  $C = 1.3 \times 10^{-17}$ .

(b) 286°K, Nyquist noise =  $1.45 \times 10^{-16} \text{ V}^2/\text{Hz}$

Fitting parameters:  $k_r = 2700 \text{ sec}^{-1}$  and  $C = 3.7 \times 10^{-18}$ ,

(c) 297°K, Nyquist noise =  $1 \times 10^{-16} \text{ V}^2/\text{Hz}$ ,

Fitting parameters:  $k_r = 4500 \text{ sec}^{-1}$  and  $C = 1 \times 10^{-18}$ .

(d) 307°K, Nyquist noise =  $7.32 \times 10^{-17} \text{ V}^2/\text{Hz}$ ,

Fitting parameters:  $k_r = 5600 \text{ sec}^{-1}$  and  $C = 4.5 \times 10^{-19}$ .

Figure 2. Rate constant versus temperature; the solid line is fitted to Equation (3).

Figure 3. A typical current noise spectrum (0.45 microamperes at 10 volts) and post-current spectra after 15 and 48 hours. The solid lines represent Equation (7) for  $k_r = 4500 \text{ sec}^{-1}$ , Nyquist noise =  $1 \times 10^{-16} \text{ V}^2/\text{Hz}$ , and  $C' = 5 \times 10^{-4}$ ,  $2.4 \times 10^{-4}$ , and  $8 \times 10^{-6}$  for the 0.45  $\mu\text{A}$ , 15 hour and 48 hour data respectively.

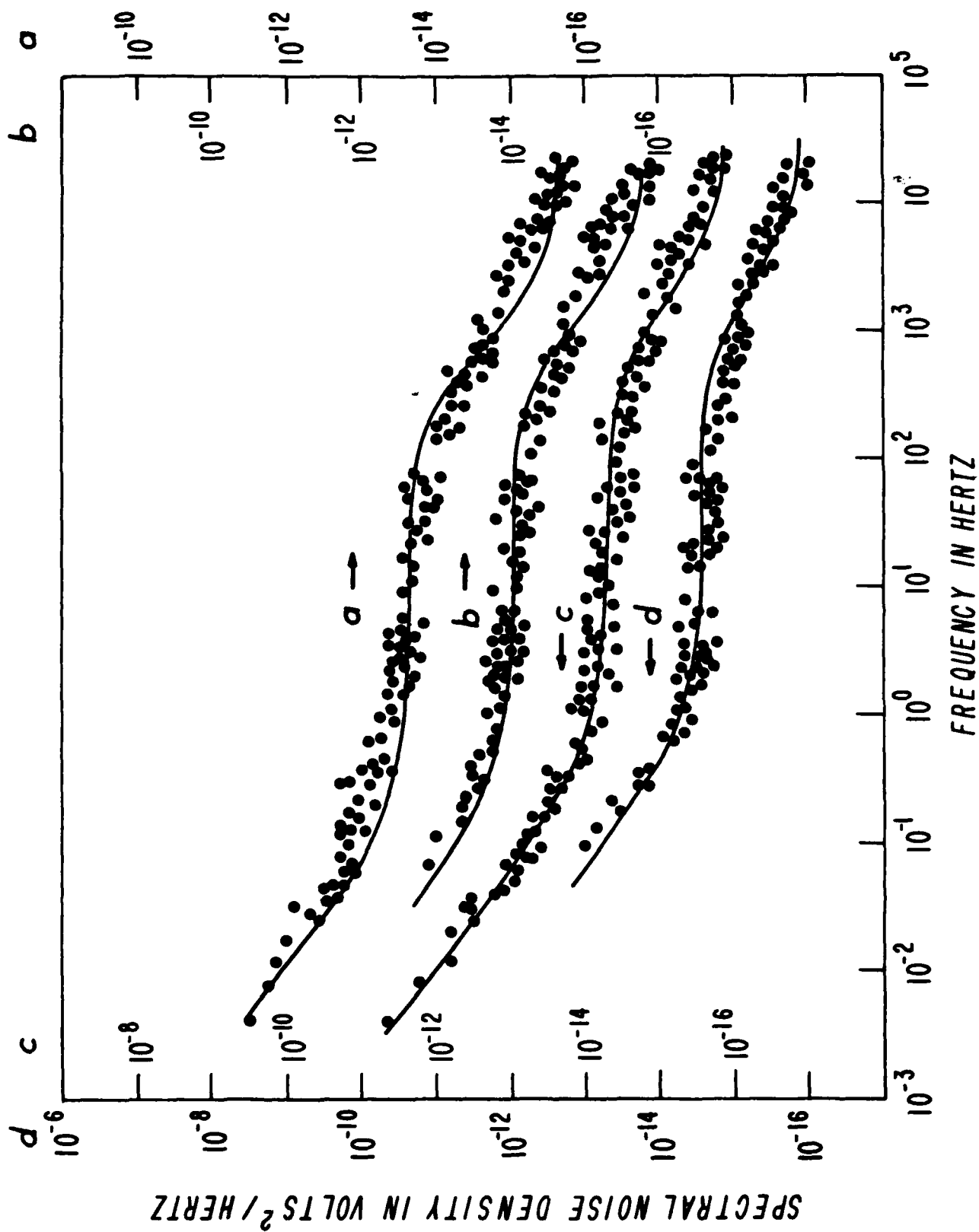


Figure 1

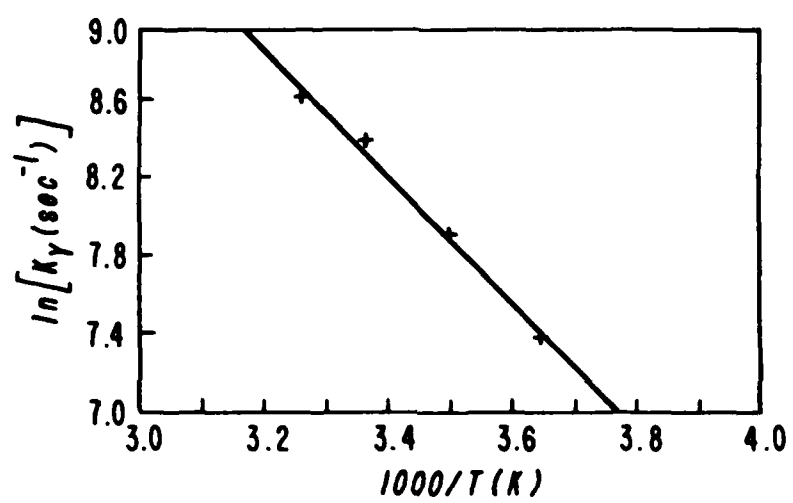


Figure 2



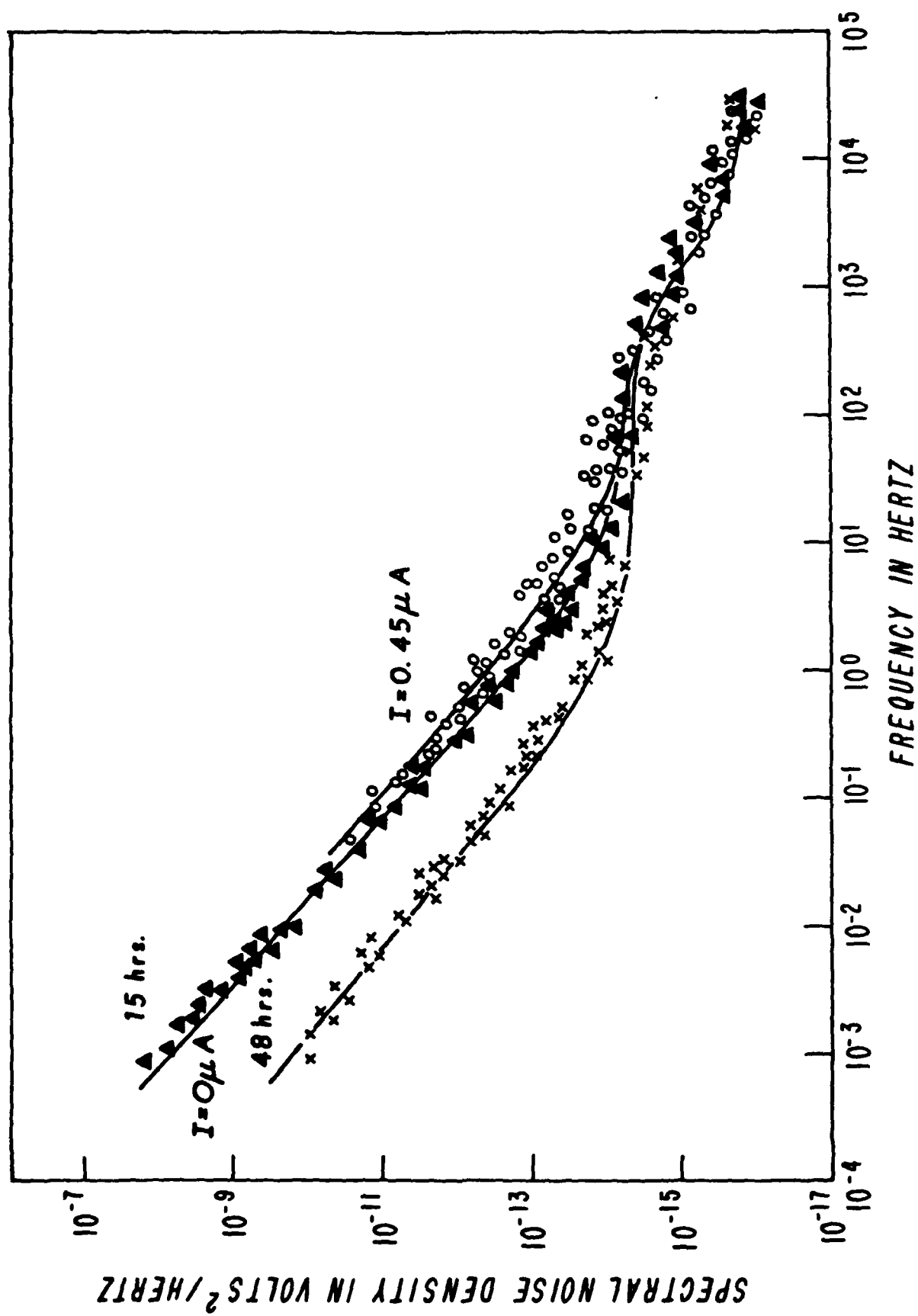


Figure 3